To: Naranjo, Eugenia[Naranjo.Eugenia@epa.gov]
Cc: Clifford Firstenberg[Clifford.Firstenberg@tierra-inc.com]; Len Warner[lwarner@louisberger.com]; AccardiDey, AmyMarie[aaccardidey@louisberger.com]
From: Carlie Thompson
Sent: Wed 3/18/2015 4:39:37 PM
Subject: RE: Comments on Tierra Sediment Pre-Program PE Report

Eugenia,

Thank you for providing additional information regarding the pesticides PE. As discussed, I've provided the questions I have regarding the pesticides, metals and butyltins tissue PEs. Below that, I've provided responses to the comments on the Sediment PE Report.

AmyMarie – if it would be helpful to discuss these, please feel free to give me a call

I've had a chance to look through some of the CPG's reports and am a little confused about the response regarding the CPG's pesticides PE performance. In the Draft 2010 Small Forage Fish Tissue Chemistry Data Report, the CPG reported "All 2,4'-DDE, 2,4'-DDT, heptachlor, and oxychlordane results were qualified as estimated (J- and UJ-qualified) because the associated CRM recovery was low. Similarly, 60% of the samples had 4,4'-DDT results qualified as estimated (J- and UJ-qualified) because the associated CRM recovery was low." This appears to me that they had some difficulty meeting the MPC in their QAPP. Their QAPP states NIST SRM 1974b as you mentioned, but I was unable to confirm either in their report or the data validation reports if that was the CRM they analyzed. Is there any documentation as to which CRM was analyzed with tissue samples? Also, since the certified values for NIST 1974b were not determined using HRGC/HRMS, the specified method for pesticides, we looked into alternatives and found NIST 1946c, which Malcolm Pirnie analyzed, and NRC CARP-2. We would like to use the NRC CARP-2 as the PE for the evaluation of pesticides since the analytical procedures used to develop the certified values include HRGC/HRMS to a larger degree than NIST 1946c. NRC CARP-2 is the same material used for the evaluation of PCB congeners and PCDDs/PCDFs.

We also had a question about the metals PE for tissue. CPG's QAPP identified the use of NRC DORM-3 and NRC TORT-2 for metals (Attachment Q of the October 2009 Benthic QAPP). We didn't have any concerns with TORT-2 but wondered about DORM-3. The CPG's Draft 2010 Small Forage Fish Tissue Chemistry Data Report in Section 5.2.2 showed that 100% of chromium results were qualified due to low and high recoveries of chromium in the CRM. I was unable to confirm either in their report or the data validation reports which CRM was analyzed. Is there any documentation as to which CRM was analyzed with tissue samples? Did USEPA's labs analyze the same PE samples? Were there any problems meeting the measurement

performance criteria?

Another item I found while reviewing the Draft 2010 Forage Fish Tissue Report was that a CRM was mentioned for butyltins. CRMs were not included in Attachment Q of the October 2009 Benthic QAPP. Do you know which CRM the CPG analyzed? Did USEPA analyze a butyltins tissue PE, if so which one was analyzed? The Forage Fish Report states "All tributyltin, dibutyltin, and monobutyltin results were qualified as estimated (J- or UJ-qualified) because associated CRM recoveries were less than the control limit of 75%." If USEPA analyzed a butyltins tissue PE, were there similar issues?

Responses to Sediment PE Report Comments

1. The measurement performance criteria used for the evaluation of the pesticides PE were the acceptance limits provided by the manufacturer. The intent of the footnote was to inform the reader that the acceptance limits shown, i.e., those provided by the manufacturer, were calculated using criteria specified by NELAC versus the footnote used on other tables referring the reader back to the QAPP where fixed ranges were provided (e.g., +/- 25% of the certified value). The referenced footnote will be changed to "The acceptance limits are defined on Worksheet #12-2 of the Crab and Clam Sampling and Analysis QAPP Rev. 3a, August 2014." to match other tables and to eliminate confusion.

While reviewing this comment we found that the units on Table 3.3-1 (pesticides) were incorrectly written as ug/kg. The units of the values in the table are pg/g so the table headers will be corrected. Also the acceptance limits for Endrin should be 50000 - 201000 instead of 36200 - 398000; this does not affect the results of the evaluation but will be corrected in the report.

2. As requested, Tierra will work with the laboratory to report the co-eluting PAH compounds as single chemicals in the MEDDs. The USEPA Region 2, Electronic Data Deliverable Valid Values Reference Manual (July 2014) has the following chemical names and CAS numbers in Table A-15 Analyte. Please confirm these are appropriate for reporting the co-eluting compounds. The following sentence will be added to the end of the referenced paragraph, "These results will be reported in the MEDD as 'benzo(j)+(k)fluoranthene' and 'dibenzo(a,h)anthracene and dibenzo(a,c)anthracene,' respectively, consistent with USEPA's

Valid Values Reference Manual (USEPA 2014)." The full reference for USEPA 2014 will also be added to the References section.

Chemical_Name	**Cas_rn**
Benzo(j)+(k)Fluoranthene	207-08-9-JK
Dibenzo(a,h)anthracene and dibenzo(a,c)anthracene	DIBENAH-AC/ANTH

3. In this case, the measurement performance criteria used for the evaluation of the metals PE were the acceptance limits provided by the manufacturer (see attached certificate). Although the measurement performance criteria in the QAPP were 70-130% recovery, since the manufacturer provided calculated PT Performance Acceptance Limits (based on regression equations and fixed acceptance criteria specified in the NELAC proficiency testing requirements), it seemed more prudent to use these limits rather than the arbitrary 70-130% recovery in the QAPP. The measurement performance criteria in the QAPP were specified prior to the purchase of this metals PE sample and receipt of the PE certificate. Should we provide a Protocol Modification Form to document this change? The referenced footnote will be changed to "The acceptance limits on Worksheet #12-2 of the Crab and Clam Sampling and Analysis QAPP Rev. 3a, August 2014 are defined as 70-130% recovery. However, the acceptance limits were modified to use limits specified by the manufacturer. These were the PT Performance Acceptance Limits in the Certificate of Analysis. The PT Performance Acceptance Limits were calculated by the manufacturer using the regression equations and fixed acceptance criteria specified in the NELAC proficiency testing requirements."

4. As discussed, sediment results for PCB-95, benzo(a)pyrene, and perylene will be qualified. The following sentence will be inserted as the 3rd sentence in the Conclusions section for clarification "Sediment results for PCB-95, benzo(a)pyrene and perylene will be qualified." These issues and subsequent actions have been closely coordinated with Tierra's data validator.

Thanks,

Carlie

From: Naranjo, Eugenia [mailto:Naranjo.Eugenia@epa.gov]

Sent: Wednesday, March 04, 2015 8:43 AM
To: Carlie Thompson
Cc: Clifford Firstenberg; Len Warner; AccardiDey, AmyMarie
Subject: FW: Comments on Tierra Sediment Pre-Program PE Report

Carlie,

AmyMarie prepared the information below in response to your question as to whether the CPG or Berger experienced difficulties with fish tissue PE analysis for pesticides during the 2009 Lower Passaic River effort. Apparently both the CPG and Berger used a different certified reference material than Tierra is currently using and did not experience difficulties meeting the pesticide acceptance criteria. AmyMarie also has some questions and comments on the attached report, which are provided below. Please feel free to contact me and/or AmyMarie with any questions.

eugenia

In response to Carlie's request, I investigated the 2010 tissue performance evaluation samples. Tierra is currently analyzing NIST SRM 1974C and reported issues with the pesticide analysis.

In 2010, the CPG analyzed NIST SRM 1974B, which is an earlier version of this reference material (refer to Appendix Q of the October 2009 Benthic QAPP). I do not have any documentation from the CPG of a nonconformance for pesticides from their lab Maxxam Analytical. According to Benthic QAPP Worksheet 28, PE samples were analyzed with every batch. If the PE exceeded the measurement performance criteria, the corrective actions were to reanalyze as necessary and then flag data accordingly. The PE results are available in the CPG database.

Malcolm Pirnie analyzed NIST SRM 1946c with each batch of split samples; the results were within the Oversight QAPP measurement performance criteria for pesticides.

I also read through Tierra's Sediment PE Technical Memorandum (dated January 23, 2015). I have a few comments on this document:

1. Page 6, Table 3.3-1, Footnote B: The Tierra Crab-Clam QAPP states that the measurement performance criteria for pesticides will be the range specified by the manufacturer. Table 3.3-1, Footnote B suggests that an alternative criterion was used. Please justify the change in acceptance criterion and

provide the regression equations used.

2. Page 8, Top Paragraph on PAH: To avoid potential confusion in interpretation of the data, Tierra's laboratory should report the co-eluting PAH compounds as "benzo(k/j)fluoranthene" and "dibenzo(a,h/a,c)anthracene." A co-elution note in the database will likely be lost during data manipulations.

3. Page 9, Table 3.7-1, Footnote B: The Tierra Crab-Clam QAPP states that the measurement performance criteria for metals will be +/- 30% of the certified value. Table 3.7-1, Footnote B suggests that an alternative criterion was used. Please justify the change in acceptance criterion and provide the regression equations used.

4. General Comment: Tierra demonstrated that their laboratories failed to meet the measurement performance criteria for PCB95, benzo(a)pyrene, and perylene for sediments. Please clarify if these compounds will be flagged or if the failures communicated to the data validator.

Regards

AM